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COMPLETE SPECIFICATION

Paper coating compositions.

We, BADISCHE ANILIN-& SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to paper coating compositions, especially paper coating compositions for the production of printing papers. More particularly it relates to the type of synthetic binder contained in the paper coating compositions.

Although only small amounts of binders, usually 5 to 30% by weight on the amount of pigment, are contained in the coating compositions, the binders substantially influence the processing properties of the compositions and the quality of the coated papers. The coating compositions should be stable when employed in the usual coating methods including the knife coating method and should not tend to form deposits, e.g. on the roller. In view of the high speeds of modern high-performance coating machines the coating compositions should have a high solids content in order to ensure that the drying capacity of the machine is sufficient. Nevertheless the coating compositions should have good flow and be stable to mechanical stress, e.g. shear stress and the applied coating should exhibit good pigment binding power.

It has been known for some time that aqueous dispersions of acrylic ester copolymers can be used as synthetic binders either alone or together with natural binders, such as starch, casein and soya protein. However, they often exhibit insufficient shear stability in high-speed machines and inadequate compatibility with certain pigments, e.g. satin white. Moreover, the viscosity of starch coating compositions which contain such synthetic binders is undesirably high. Furthermore, it is known from British Patent Specification No. 987,404 and Canadian Patent Specification 733,172 that mixtures of acrylic ester and vinyl ester copolymers with acrylic acid/acrylic ester copolymers can be used as synthetic binders for paper coating compositions. Although papers coated with these compositions have valuable properties, alkaline coating compositions prepared with the said binders are often very viscous, their viscosity increasing as the amount of acrylic acid copolymer added is increased.

We have now found that paper coating compositions which, per 100 parts by weight of finely divided pigment, contain 1 to 25 parts by weight of a synthetic binder consisting of a mixture of a copolymer A having a glass temperature of from −60 to +30°C and a water-soluble ammonium, amine or alkali-metal salt of a copolymer B prepared from acrylic esters and ethylenically unsaturated carboxylic acids with 3 to 5 carbon atoms, have particularly advantageous properties when they contain, as copolymers A, copolymers derived from
(1) 20 to 70% by weight of styrene and/or acrylonitrile, 80 to 30% by weight of esters of acrylic acid and/or methacrylic acid with alkanols having 1 to 12 carbon atoms and 0 to 10% by weight of other ethylenically unsaturated monomers or from
(2) 20 to 70% by weight of styrene and/or acrylonitrile, 20 to 80% by weight of butadiene, 0 to 30% by weight of esters of

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acrylic acid and/or methacrylic acid with alkanols having 1 to 12 carbon atoms, and 0 to 10% by weight of other ethylenically unsaturated monomers and, as copolymers B, copolymers having a K value of 12 to 40 and derived from 60 to 95% by weight of esters of acrylic acid and/or methacrylic acid with alkanols having 1 to 8 carbon atoms, 5 to 40% by weight of ethylenically unsaturated carboxylic acids, and 0 to 10% by weight of other ethylenically unsaturated monomers, the mixture of copolymers A and B containing from 0.5 to 10% by weight of copolymer B. The new paper coating compositions may additionally contain natural binders and/or the usual additives.

The synthetic binder mixture contained in the coating compositions is particularly suitable for use together with natural binders, such as starch, casein or soya protein. Starch is preferred as natural binder. The natural binders may be replaced wholly or in part by synthetic binders other than the copolymers A and B to be used according to the invention.

In conjunction with a natural binder 1 to 15 parts by weight, preferably 3 to 12 parts by weight, of the mixture of copolymers A and B may be used per 100 parts by weight of pigment. In the absence of a natural binder 1 to 25 parts by weight, preferably 7 to 15 parts by weight, of the synthetic binder mixture is used per 100 parts by weight of pigment. The total amount of natural and synthetic binder should be 5 to 30 parts, preferably 7 to 25 parts, by weight per 100 parts by weight of pigment.

The copolymer A specified under (1) contains 20 to 70%, particularly 30 to 50%, by weight of styrene and/or acrylonitrile units, styrene being preferred, and 80 to 30%, particularly 70 to 50%, by weight of units of esters of acrylic and/or methacrylic acid. Examples of suitable esters of these acids with alkanols having 1 to 12, particularly 2 to 8, carbon atoms are ethyl acrylate, n-butyl acrylate, isobutyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, n-dodecyl acrylate and the corresponding methacrylates. n-Butyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate are preferred.

The copolymer A specified under (2) may be used instead of copolymer A (1). It may for example only contain 20 to 80% by weight of butadiene units and 20 to 70% by weight of styrene and/or acrylonitrile units, styrene being preferred. Copolymers A (2) which are derived only from butadiene and styrene or acrylonitrile are very suitable for the paper coating compositions according to the invention. However, copolymers A (2) which additionally contain 5 to 30% by weight of units of acrylic and/or methacrylic esters of alkanols having 1 to 12 carbon atoms are much superior, particularly with regard to pigment binding power (measured according to the I.G.T. picking test, cf. G. A. Hemstock and J. W. Swanson, Tappi *40*, 794 (1957)) and resistance to aging. Copolymers A (2) which contain 30 to 40% by weight of butadiene units, 40 to 60% by weight of styrene units and 10 to 25% by weight of units of esters of acrylic and/or methacrylic acid with alkanols having 1 to 8 carbon atoms (n-butyl acrylate and isobutyl acrylate being preferred) are of particular interest.

Examples of suitable other ethylenically unsaturated compounds which may be used in amounts of 0 to 10% by weight in the preparation of copolymers A (1) and (2) are the usual comonmers, particularly vinyl acetate, vinyl propionate, butadiene (for copolymers A (1)), dialkyl maleates, dialkyl fumarates, vinyl chloride and vinylidene chloride. The copolymers A should preferably contain 0.1 to 10%, particularly 0.5 to 5%, by weight of units of hydrophilic polar monomers, such as ethylenically unsaturated carboxylic acids having 3 to 5 carbon atoms and/or their amides, mono-N-alkylamides, di-N-alkylamides, N-methylolamides or etherified N-methylolamides, e.g. acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, acrylamide, N-methylolmethacrylamide, maleamide, maleic diamide or itaconic acid half-ester. Particularly suitable monomers of this kind are acrylic acid, methacrylic acid, acrylamide and methacrylamide. It is also possible to use mixtures of the said monomers in the polymerization. Moreover, mixtures of a copolymer A (1) and a copolymer A (2) may be used for preparing the paper coating compositions.

The glass temperature of the copolymers A should be between —60 and +30°C., preferably between —30 and +10°C. For details regarding the glass temperature reference is made to L. E. Nielson, Mechanical Properties of Polymers, New York, 1962, page 11 et seq.

Polymers which do not fulfill the above requirement are not suitable for preparing the binders to be used in accordance with the invention. For example, a copolymer derived from 60% by weight of styrene, 38% by weight of ter.-butyl acrylate and 2% by weight of acrylic acid has a glass temperature of more than 30°C and is therefore unsuitable as copolymer A. The same applies to a copolymer derived from 60% by weight of acrylonitrile, 18% by weight of tert.-butyl acrylate, 20% by weight of butadiene and 2% by weight of acrylic acid. In contrast to this, copolymers A derived from 30 to 40% by weight of butadiene, 60 to 40% by weight of styrene, 10 to 25% by weight of n-butyl acrylate and/or isobutyl

acrylate, 1 to 5% by weight of acrylic acid and/or methacrylic acid, and 0.5 to 5% by weight of acrylamide and/or methacrylamide are particularly suitable and are therefore preferred. Copolymers A derived from 40 to 60% by weight of n-butyl acrylate and/or isobutyl acrylate, 60 to 40% by weight of styrene, 1 to 5% by weight of acrylic acid and/or methacrylic acid and 0.5 to 5% by weight of acrylamide and/or methacrylamide are also very suitable.

The copolymers A are usually produced by polymerization of the monomers in aqueous emulsion by conventional methods, preferably using the usual anionic and/or nonionic emulsifiers. Examples of suitable emulsifiers are potassium n-dodecyl sulfonate, sodium isooctylbenzene sulfonate, the potassium salt of the sulfuric acid halfester of lauroyl alcohol, and p-isooctylphenol or sodium laurate reacted with 20 to 30 moles of ethylene oxide; they are usually used in amounts of about 0.5 to 5% by weight with reference to the monomers.

Conventional free-radical forming substances, such as peroxides, persulfates and azo compounds, e.g. potassium persulfate, cumene hydroperoxide and azodiisobutyric diamide, may be used as polymerization initiators in amounts of about 0.02 to 2% by weight with reference to the monomers. The polymerization may be carried out at the usual temperatures, e.g. at from 50 to 90°C. The temperatures may be lower if redox catalysts or activated initiator systems, e.g. a system of potassium persulfate and ascorbic acid, sodium hydroxymethane sulfinate or triethanolamine, are used. It is preferred to use dispersions with a solids content of 20 to 60% by weight.

In accordance with the invention the copolymers B should have a K value of from 12 to 40 and be derived from 60 to 95%, particularly 70 to 90%, by weight of an ester of acrylic acid and/or methacrylic acid and 5 to 40%, particularly 10 to 30%, by weight of ethylenically unsaturated carboxylic acids with 3 to 5 carbon atoms. Examples of suitable esters of acrylic acid and/or methacrylic acid with alkanols having 1 to 8, particularly 2 to 4, carbon atoms are methyl methacrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate and n-octyl acrylate. Methyl acrylate, ethyl acrylate, isobutyl acrylate, n-butyl methacrylate and particularly n-butyl acrylate are preferred. Among ethylenically unsaturated carboxylic acids with 3 to 5 carbon atoms, such as maleic acid, fumaric acid and itaconic acid, acrylic acid and methacrylic acid are preferred. It is also possible to use mixtures of the said monomers in the preparation of the copolymers. Copolymers B which, in addition to the said types of monomer, contain 0 to 10%, particularly 2 to 6%, by weight of acrylamide and/or methacrylamide units are preferred. It is possible to vary the properties of the copolymers within a narrow range by additionally using 0 to 10% by weight of other monomers, such as styrene, acrylonitrile and vinyl acetate, diolefins, e.g. butadiene and isoprene, and esters and half-esters of ethylenically unsaturated dicarboxylic acids, e.g. diethyl itaconate, dibutyl fumarate and mono-2-ethylhexyl maleate, and thus to adapt them to make the coating compositions or the coated papers meet special requirements.

The copolymers B may be produced in conventional manner by emulsion or solution polymerization. Copolymers B which have been produced by polymerization of the monomers in organic solvents in which the monomers and the copolymers are soluble, particularly alkanols, e.g. ethanol, propanol and butanol, are preferred. The solvents can be removed by distillation and the copolymers B can be converted into their aqueous solutions after neutralization with ammonia or other bases. Examples of suitable catalysts for the production of the solution polymers are benzoyl peroxide, lauroyl peroxide or azodiisobutyronitrile. In general the polymerization temperature ranges from 60°C to the boiling point of the solvent used. For regulating the molecular weight, i.e. in order to obtain the above-mentioned K values, the usual chain transfer agents, e.g. n-dodecyl mercaptan, cyclohexene or carbon tetrabromide, may be used in the production of copolymers B in amounts of from about 0.05 to 0.5% by weight with reference to the monomers. The K values of the copolymers (according to H. Fikentscher, Cellulosechemie *13* (1932), pages 58 ff., measured in a 1% aqueous solution neutralized with ammonia) should always be from 12 to 40, particularly from 15 to 25.

The paper coating compositions according to the invention contain a mixture of a copolymer A and a copolymer B. The copolymer mixture should contain 90 to 99.5% by weight of a copolymer A (solid) and 10 to 0.5% by weight of a copolymer B (solid). Copolymer mixtures which contain 94 to 98% by weight of a copolymer A and 6 to 2% by weight of a copolymer B are preferred. The binder may contain several copolymers A and/or several copolymers B.

The mixing of the copolymers may be effected before or during the preparation of the coating compound. It is also immaterial for the properties of the coating compound or the coated paper in what sequence the components of the coating composition are mixed. It is however advantageous to mix the aqueous dispersion of copolymer A with the aqueous solution of copolymer B in the desired relative proportions before the prep-

aration of the coating composition. The finished mixture can be stored because the copolymers A and B have excellent compatibility with each other and copolymer B greatly increases the stability of the dispersion of copolymer A. The most favorable pH value of the mixture is from 6 to 10; it is preferred to adjust the pH value with ammonia.

Pigments conventionally used in paper coating, e.g. clay, titanium dioxide and satin white, may be employed for preparing the new coating compositions. The coating compositions may also contain auxiliaries and alkali, e.g. sodium hydroxide or potassium hydroxide, preferably ammonia.

The paper coating compositions may be applied to raw stock by any conventionally used method. Their particular advantage lies in their good rheological properties and their high shear stability which makes it possible to apply them by the particularly simple knife coating method. They are distinguished by uniform flow, good water resistance and smoothness of the finished coating. These advantageous properties of the coating compositions were not foreseeable.

As compared with known paper coating compositions which, in addition to natural binders, contain acrylic ester copolymers or butadiene copolymers either alone or in admixture with acrylic acid copolymers, the coating compositions according to the invention have a distinctly lower viscosity (cf. Examples 1 to 7 and comparative examples); the viscosity decreases as the amount of copolymer B is increased. Their low viscosity makes it possible to apply them by machinery operated at very high speeds to produce valuable papers with excellent printing qualities.

The invention is further illustrated by the following Examples in which parts and percentages are by weight. The viscosity figures indicated in centipoises (cp) were measured at 20°C with a Brookfield viscometer at 100 r.p.m.

The preparation of a dispersion of the copolymer A used in Examples 1 to 3 is carried out as follows: 1,050 parts of styrene 1,050 parts of n-butyl acrylate, 42 parts of acrylic acid and 10 parts of sodium vinyl sulfonate are emulsified in 1,960 parts of water in a stirred vessel together with 42 parts of an adduct of 25 moles of ethylene oxide to p-isooctyl phenol, 84 parts of the same adduct esterified with sulfuric acid, and 9.6 parts of potassium persulfate. In the course of 4 hours this mixture is introduced at 80 to 85°C while stirring into 180 parts of water heated to 80°C. Then another 1.5 parts of potassium persulfate in 60 parts of water is added and polymerization is completed at 85°C. An approximately 50% copolymer dispersion is obtained. The glass temperature of the copolymer A used in Examples 1 to 3 is 15°C., that used in Examples 6 is —5°C and that used in Example 13 is 0°C. The glass temperatures of the copolymers A of the remaining Examples are from —60°C to +30°C.

The preparation of a solution of copolymer B is carried out chiefly by the methods of solution polymerization conventionally used in industry. In the case of Examples 1 to 3 the procedure was as follows: 100 parts of isobutanol and 1 part of benzoyl peroxide is heated in a polymerization vessel to about 100°C while stirring. Then a mixture of 180 parts of isobutanol, 302 parts of butyl acrylate, 101 parts of acrylic acid and 17 parts of acrylamide are introduced together with 2 parts of benzoyl peroxide and 0.7 part of n-dodecyl mercaptan. The reaction temperature is maintained at the same temperature for 1 hour and the isobutanol is then distilled off. The polymer melt is cooled to about 90°C. neutralized with ammonia water and diluted with water to a solids content of 50%, a clear viscous solution being formed. The polymer has a K value of 19. The preparation of solutions of copolymers B in Examples 5, 8, 11, 13 and 15—19 was carried out in an analogous manner, and the copolymers B are accordingly used in salt form.

EXAMPLES 1 to 3

For preparing a 64% coating composition 100 parts of china clay is stirred into a solution of 0.3 part of tetrasodium pyrophosphate in 43 parts of water by means of an impeller. 29.3 parts of a 37.5% dispersion of degraded potato starch in water and 6 parts of a 50% mixture of the dispersion of copolymer A and the solution of copolymer B are added. The coating composition is adjusted to pH 8 with caustic soda solution.

EXAMPLE 1

The mixture of copolymers A and B comprises 96% of copolymer A and 4% of copolymer B with reference to the solids. The resultant coating composition has a viscosity of 8,000 cp at 20°C.

EXAMPLE 2

The mixture of copolymers A and B comprises 98% of copolymer A and 2% of copolymer B with reference to the solids. The resultant coating composition has a viscosity of 20,000 cp at 20°C.

EXAMPLE 3

The mixture of copolymers A and B comprises 99% of copolymer A and 1% of copolymer B with reference to the solids. The resultant coating composition has a viscosity of 38,000 cp at 20°C.

Comparative Example referring to Examples 1 to 3.

The coating composition is prepared as described in Examples 1 to 3, except that 6

parts of a 50% dispersion of copolymer A is added as synthetic binder, i.e. no copolymer B is used. The resulting coating composition has a viscosity of 82,000 cp at 20°C.

EXAMPLE 4

A 64% starch-containing paper coating composition is prepared as described in Examples 1 to 3. 6 parts of a 50% mixture of copolymers A and B is used as synthetic binder. Copolymer A is prepared from 33 parts of styrene, 63.5 parts of n-butyl acrylate, 1.5 parts of acrylic acid and 2 parts of methacrylamide by a conventional emulsion polymerization method. Copolymer B is the same as that used in Example 1. The mixture of copolymers A and B contains 97 parts of copolymer A and 3 parts of copolymer B (solid). The resulting coating composition has a viscosity of 12,000 cp at 20°C.

Comparative Example referring to Example 4.

A starch-containing paper coating composition is prepared as described in Example 4, but 6 parts of a 50% dispersion of copolymer A alone is used as synthetic binder. The viscosity of the resultant coating composition is 75,000 cp at 20°C.

EXAMPLE 5

A 64% paper coating composition is prepared as described in Examples 1 to 3. 6 parts of a 50% mixture of copolymers A and B is used as synthetic binder. Copolymer A is the same as that used in Example 4; copolymer B is derived from 87 parts of ethyl acrylate, 10 parts of acrylic acid and 1.5 parts of acrylamide and has a K value of 23. The mixture of copolymers A and B contains 97% of copolymer A and 3% of copolymer B. The viscosity of the coating composition is 11,500 cp at 20°C.

EXAMPLE 6

For preparing a casein-containing coating composition 20 parts of casein is peptized with 1.1 part of sodium hydroxide in 78.9 parts of water at 50°C. 100 parts of china clay and 52 parts of water are introduced in portions into 15 parts of the casein solution thus obtained by means of an impeller. 24 parts of a 50% mixture of copolymers A and B is added to this mixture.

As described above, copolymer A is prepared by emulsion copolymerization from the following monomers: 12 parts of styrene, 18 parts of acrylonitrile, 63.5 parts of n-butyl acrylate, 1 part of acrylic acid and 0.5 part of acrylamide. Copolymer B is the same as that used in Example 1. The coating composition is adjusted to pH 11 with caustic soda solution and has a viscosity of 1,700 cp at 20°C.

Comparative Example referring to Example 6.

A casein-containing coating composition is prepared as described in Example 6, but 24 parts of a 50% dispersion of copolymer A alone is used as synthetic binder. The viscosity of the resultant coating composition is 2,750 cp.

EXAMPLE 7

A starch-containing 64% paper coating composition is prepared as described in Example 1 except that the copolymer mixture of Example 6 is used. The viscosity of the coating composition is 9,500 cp at 20°C.

Comparative Example 1 referring to Example 7.

If the procedure of Example 7 is followed except that the copolymer A dispersion according to Example 6 is used alone as synthetic binder, the viscosity of the resultant coating composition is 90,000 cp.

Comparative Example 2 referring to Example 7.

The procedure of Example 7 is followed except that a mixture of 97 parts of the copolymer A dispersion according to Example 6 and 3 parts of a solution of copolymer B having a K value of 75 (measured in cyclohexanone) is used as synthetic binder. The resultant coating composition has a viscosity of 130,000 cp.

EXAMPLE 8

To prepare a coating composition having a solids content of 64%, 100 parts of china clay is introduced with vigorous stirring into a solution of 0.8 part of tetrasodium pyrophosphate and 11 parts of oxidatively degraded starch (dissolved at about 85°C) in 50 parts of water. A mixture of 6 parts of a 50% dispersion of a copolymer A derived from 55 parts of styrene, 28 parts of butadiene, 20 parts of n-butyl acrylate, 2 parts of acrylic acid and 1.5 parts of methacrylamide and 0.48 part of a 25% solution of a copolymer B derived from 75 parts of n-butyl acrylate, 20 parts of acrylic acid and 5 parts of acrylamide is then added with stirring. The copolymer B has a K value of 19. The coating composition is adjusted to pH 8 with 10% caustic soda solution and the solids content to 64% by the addition of water. This viscosity of the coating composition is 22,000 cp at 20°C (measured by means of a Brookfield viscometer at 20 r.p.m.).

A coating composition prepared in the same way but without using copolymer B has a viscosity of 176,000 cp.

EXAMPLE 9

A coating composition is prepared as described in Example 1, but using as binder a mixture of 6 parts of a 50% dispersion of a copolymer A derived from 50 parts of styrene, 35 parts of butadiene, 15 parts of ethyl acrylate, 2 parts of acrylic acid and 1 part of methacrylamide and 0.42 part of a 25% solution of the copolymer B used in Example 1. The viscosity of the mixture is

39,000 cp.

A coating composition prepared without using copolymer B has a viscosity of 350,000 cp.

EXAMPLE 10

A coating composition is prepared as described in Example 1 but using as binder a mixture of 8 parts of a 50% dispersion of a copolymer A derived from 55 parts of styrene, 45 parts of butadiene, 2.5 parts of acrylic acid and 0.5 part of methacrylamide and 0.50 part of a 25% solution of the copolymer B used in Example 1. The viscosity of the coating composition is 18,000 cp.

EXAMPLE 11

A coating composition is prepared as described in Example 1 but using as binder a mixture of 6 parts of a 50% dispersion of the copolymer A used in Example 1 and 0.45 part of a 25% solution of a copolymer B derived from 87 parts of ethyl acrylate, 10 parts of acrylic acid and 1.5 parts of acrylamide, the mixture having a K value of 23. The coating composition has a viscosity of 17,000 cp.

EXAMPLE 12

25 parts of the mixture of copolymers A and B indicated in Example 1 is introduced with vigorous stirring into a mixture of 100 parts of china clay, 45 parts of water and 15 parts of a 20% casein solution (dissolved with caustic soda solution). The pH of the coating composition is adjusted to 11 with caustic soda solution and the solids content to 60% by the addition of water. The viscosity is 1,700 cp at 20°M (measured with a Brookfield viscometer at 20 r.p.m.).

If the coating composition is prepared without using a copolymer B, the viscosity is 2,800 cp.

EXAMPLE 13

A coating composition is prepared from 70 parts of china clay, 30 parts of satin white (100%), 52.5 parts of a 20% casein solution and a mixture of 22.6 parts of a 50% dispersion of a copolymer. A derived from 30 parts of styrene, 15 parts of acrylonitrile, 35 parts of butadiene, 20 parts of isobutyl acrylate, 2.5 parts of acrylic acid and 1.0 part of methacrylamide with 1.6 parts of a 25% solution of a copolymer B derived from 75 parts of n-butyl acrylate, 20 parts of acrylic acid and 5 parts of acrylamide, the copolymer mixture having a K value of 19. The pH of the coating composition is adjusted to 11 and the solids content to 35%. The coating composition has a viscosity of 167 cp.

If the coating composition is prepared without using copolymer B, the viscosity is 265 cp.

EXAMPLE 14

A 64% starch-containing paper coating composition is prepared as described in Example 1 but using as synthetic binder a mixture of 96% of a copolymer A derived from 50 parts of styrene, 50 parts of 2-ethylhexyl acrylate, 2 parts of methacrylic acid and 1 part of methacrylamide and 4% of a copolymer B, K value 31.8, derived from 50 parts of n-butyl acrylate, 25 parts of methyl methacrylate, 20 parts of acrylic acid and 5 parts of acrylamide. The viscosity of the coating composition is 10,000 cp at 20°C.

In contrast to this, a paper coating composition which contains only copolymer A instead of the mixture of copolymers A and B has a viscosity of 18,000 cp.

EXAMPLE 15

A 64% starch-containing paper coating composition is prepared as described in Example 1 but using a synthetic binder which contains, with reference to its solids content, 96% of a copolymer A derived from 40 parts of styrene, 40 parts of ethyl acrylate, 12 parts of n-butyl acrylate, 8 parts of dibutyl fumarate, 1.5 parts of acrylic acid and 0.5 part of methacrylamide and 4% of a copolymer B, K value 31.8 derived from 50 parts of n-butyl acrylate, 25 parts of methyl methacrylate, 20 parts of acrylic acid and 5 parts of acrylamide. Copolymer A is used in the form of a 50% aqueous dispersion, copolymer B in the form of a 20% aqueous solution. The paper coating composition obtained has a viscosity of 12,000 cp at 20°C.

A paper coating composition which contains only copolymer A instead of the mixture of copolymers A and B has a viscosity of 62,000 cp.

EXAMPLE 16

A starch-containing 64% paper coating composition is prepared as described in Example 1 but using a synthetic binder which contains, with reference to its solids content, 96% of a copolymer A derived from 60 parts of n-butyl acrylate, 40 parts of styrene, 2 parts of methacrylamide, 2 parts of ethanediol monoacrylate and 2 parts of 2-chloro-3-oxypropyl acrylate and 4% of a copolymer B, K value 20, derived from 75 parts of n-butyl acrylate, 20 parts of acrylic acid and 5 parts of acrylamide. Copolymer A is used in the form of a 50% aqueous dispersion, copolymer B in the form of a 20% aqueous solution. The paper coating composition obtained is 11,000 cp at 20°C.

A paper coating composition which contains only copolymer A instead of the mixture of copolymers A and B has a viscosity of 14,000 cp at 20°C.

EXAMPLE 17

A starch-containing 64% paper coating composition is prepared as described in Example 1 but using a synthetic binder which contains, with reference to its solids content, 96% of a copolymer A derived from 60 parts of n-butyl acrylate, 40 parts of styrene,

2 parts of methacrylamide, 1.5 parts of acrylic acid and 1 part of 2-chloro-3-oxypropyl acrylate and 4% of the copolymer B used in Example 15. Copolymer A is used in the form of a 50% aqueous dispersion, copolymer B in the form of a 20% aqueous solution. The paper coating composition obtained has a viscosity of 13,000 cp at 20°C.

EXAMPLE 18

A starch-containing 64% paper coating composition is prepared as described in Example 1 but using a synthetic binder which contains, with reference to its solids content, 96% of a copolymer A having the composition indicated in Example 17 and 4% of a copolymer B, K value 21.7, derived from 40 parts of n-butyl acrylate, 30 parts of methacrylic acid, 20 parts of ethyl acrylate, 8 parts of vinyl acetate and 10 parts of acrylamide. Copolymer A is used in the form of a 50% aqueous dispersion, copolymer B in the form of a 20% aqueous solution. The paper coating composition obtained has a viscosity of 14,200 cp at 20°C.

EXAMPLE 19

A starch-containing 64% paper coating composition is prepared as described in Example 1 but using a synthetic binder which contains, with reference to its solids content, 96% of a copolymer A having the composition indicated in Example 17 and 4% of a copolymer B having the composition indicated in Example 16. Copolymer A is used in the form of a 50% aqueous dispersion, copolymer B in the form of a 20% aqueous solution. The paper coating composition obtained has a viscosity of 11,500 cp at 20°C.

A coating composition which contains only copolymer A instead of the mixture of copolymers A and B has a viscosity of 182,000 cp at 20°C.

WHAT WE CLAIM IS:—

1. Paper coating compositions containing, per 100 parts by weight of finely divided pigment, 1 to 25 parts by weight of a synthetic binder consisting of a mixture of a copolymer A having a glass temperature of from —60°C to +30°C and a water-soluble ammonium, amine or alkali metal salt of a copolymer B derived from acrylic esters and ethylenically unsaturated carboxylic acids with 3 to 5 carbon atoms, wherein copolymer A is derived from

(1) 20 to 70% by weight of styrene and/or acrylonitrile, 80 to 30% by weight of esters of acrylic acid and/or methacrylic acid with alkanols having 1 to 12 carbon atoms, and 0 to 10% by weight of other ethylenically unsaturated monomers or from

(2) 20 to 70% by weight of styrene and/or acrylonitrile, 20 to 80% by weight of butadiene, 0 to 30% by weight of esters of acrylic acid and/or methacrylic acid with alkanols having 1 to 12 carbon atoms, and 0 to 10% by weight of other ethylenically unsaturated monomers and copolymer B has a K value of from 12 to 40 and is derived from 60 to 95% by weight of esters of acrylic acid and/or methacrylic acid with alkanols having 1 to 8 carbon atoms, 5 to 40% by weight of ethylenically unsaturated carboxylic acids, and 0 to 10% by weight of other ethylenically unsaturated monomers, the mixture of copolymers A and B containing from 0.5 to 10% by weight of copolymer B.

2. A paper coating composition as claimed in claim 1 wherein the copolymer A (1) contains 30 to 50% by weight of the styrene and/or acrylonitrile units and 70 to 50% by weight of units of esters of acrylic acid and/or methacrylic acid.

3. A paper coating composition as claimed in claim 1 wherein copolymer A (2) contains 30 to 40% by weight of butadiene units, 40 to 60% by weight of styrene units and 10 to 25% by weight of units of esters of acrylic acid and/or methacrylic acid with alkanols having 1 to 8 carbon atoms.

4. A paper coating composition as claimed in claim 3 wherein the ester of acrylic acid is n-butyl acrylate or isobutyl acrylate.

5. A paper coating composition as claimed in any of claims 1 to 4 wherein the glass temperature of copolymer A is from —30°C to +10°C.

6. A paper coating composition as claimed in any of claims 1 to 5 wherein copolymer B is derived from 70 to 90% by weight of an ester of acrylic acid and/or methacrylic acid and 10 to 30% by weight of ethylenically unsaturated carboxylic acids having three to five carbon atoms.

7. A paper coating composition as claimed in any of claims 1 to 6 wherein copolymer B contains 2 to 6% by weight of acrylamide and/or methacrylamide units.

8. A paper coating composition as claimed in any of claims 1 to 7 wherein the copolymer mixture contains 94 to 98% by weight of copolymer A and 6 to 2% by weight of copolymer B.

9. A paper coating composition as claimed in claim 1 substantially as described in any of the foregoing Examples.

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Appl. 3,275,603, 09 Apr 1981. From *Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki* 1982, (41), 44. The device consists of a horizontal cylindrical casing, a filtering component located inside the casing, a drive, lids fixed to the ends of the casing, and phase input and output branch pipes. The *lignin* [9005-53-2] discharge is improved by an increased degree of filtration by making the filtering component as a grate, placing it in the lower part of the casing and equipping it with wedge-shaped scrapers perpendicular to the grate. Blades are fixed to the scrapers and placed in the grate slits ensuring reciprocal motion.

98: 181411b **Measurement of degree of cooking of chemical pulp.** Jujo Paper Mfg. Co., Ltd. Jpn. Kokai Tokkyo Koho JP 57,199,952 [82,199,952] (Cl. G01N27/46), 08 Dec 1982, Appl. 81/83,883, 02 Jun 1981; 10 pp. In rapid measurement of the degree of cooking of unbleached pulp, Cl is added to the pulping liquor and the Kappa value of the liquor is detd. by measuring the elec. cond. or light absorption of the liquor.

98: 181412c **Delignification bleaching of cellulose pulp.** Samuelson, Hans Olof (Mo och Domsjo AB) Ger. Offen., DE 3,225,271 (Cl. D21C3/22), 07 Apr 1983, SE Appl. 81/5,552, 21 Sep 1981; 29 pp. The activation of pulp half stuff of 26–45% consistency with NO, NO_2, N_2O_4 or N_2O_3 in combination with HNO_3, and delignification with alk. O or peroxide gave bleached pulp. Thus, sulfate pine half stuff (Kappa (K) no. 33.5, and viscosity no. 1185 dm^3/kg) of 39% consistency was impregnated with 0.4 g mol HNO_3 per kg H_2O in pulp, dild. with H_2O to 30% consistency, heated to 58°, treated with 2% NO_2 for 75 min, washed with cold H_2O, dild. to 26% consistency, treated with 1.5% NaOH and bleached with O at 0.11 MPa for 60 min at 106° to give a specimen with K no. 10.8 and viscosity no. 1031 dm^3/kg.

98: 181413d **Thermomechanical wood pulp production.** Zuikov, A. A.; Osminin, E. N.; Goroshnikov, V. V.; Bobrov, A. I. (Central Scientific-Research Institute of Paper) U.S.S.R. SU 1,002,435 (Cl. D21C9/10), 07 Mar 1983, Appl. 3,375,323, 29 Dec 1981. From *Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki* 1983, (9), 100. Lignocellulosic material is steamed at elevated temp. and pressure, beaten in 2 stages and treated with a reducing agent in the 2nd stage. The physicomech. properties of the product are improved and the consumption of chems. reduced by carrying out the treatment with 10–50% of the total consumption of reducing agent, and after the beating carrying out addnl. bleaching with the rest of the reducing agent at 70–95° and a pH 4–6. $Na_2S_2O_4$ or Rongalite are used as the reducing agent.

98: 181414e **Insulating and filler material comprising cellulose fibers and clay from paper-making waste.** Neckermann, Edwin F.; Wooding, Joseph S. (American Fillers and Abrasives Co., Inc.) Can. CA 1,142,306 (Cl. C04B43/12), 08 Mar 1983, Appl. 363,580, 30 Oct 1980; 11 pp. The removal of H_2O from white H_2O of papermaking machine, milling the dry agglomerate obtained, and sieving from 3/8 in. mesh screen gave fluffy product contg. cellulose pulp with entrapped clay particles for use as insulator. Thus, 200 lb waste paper slurry (cellulose pulp and kaolin contents, 25.12% and 14.9%, resp.) which has passed through the screen of papermaking machine, was air-dried for 2 day at room temp., ~1/2 of this was run through hammer mill with 1/4 in. screen and the other 1/2 through 3/8 in. screen to give product with 25–30 lb/ft^3 bulk d.

98: 181415f **Process for producing fiberboard wherein dissolved wood matter is separated from the process water.** Roennquist, Axel G.; Berglund, Eskil; Carendi, Lars G. (KF Industri AB) Can. CA 1,140,382 (Cl. D21C7/00), 01 Feb 1983, SE Appl. 79/3,177, 10 Apr 1979; 10 pp. A process, in which the H_2O contg. dissolved wood substances from dewatering device is recycled to evaporator and defibrator, was described to produce mech. pulp of at least 60% consistency for use in the prodn. of fiberboard by preheating wood chips or sawdust with steam, difibrating, treating in cyclone, leaching, and dewatering. Thus, for the prodn. of 400 ton hardboard, the system described produced pulp of 60% consistency and discharged effluents with ~6.5 kg BOD per ton board as compared with effluent discharge having 27 kg BOD per ton board without recycling process H_2O.

98: 181416g **Treating pulp with plural oxygen stages.** Bentvelzen, Joseph M.; Crosby, Gerald D.; Torregrossa, Louis O. (Weyerhaeuser Co.) PCT Int. Appl. WO 83 00,887 (Cl. D21C9/02), 17 Mar 1983, Appl. 81/Us1186, 04 Sep 1981; 52 pp. A bleaching process is described in which a step involving treatment of cellulose pulp at 7–15% consistency with O at alk. pH and 65–121° is inserted in existing bleaching processes involving treatement by hypochlorite, peroxide, O_3, Cl or ClO_2. Thus, treatment of pulp with 22.7 kg O/ton pulp in the presence of 15.1 kg NaOH/ton at 79.5% and 517.5 kPa gage pressure reduced permanganate no. of pulp from 18.6 to 15.6.

98: 181417h **Pulp mill recovery.** Liem, Albert J. (Domtar, Inc.) U.S. US 4,377,439 (Cl. 162-30.1; D21C11/12), 22 Mar 1983, Appl. 208,666, 20 Nov 1980; 5 pp. A system is described to recover heat and chems. from black sulfite liquor by forming a fluidized bed of pellets of inorg. compds. derived from black liquor, extg. pellets from the bed and injecting them into a drier, where they are coated with cond. black liquor and dried, injecting the coated pellets into a fluidized bed, and extg. heat from the bed to maintain it at operating temps. Some of the coated pellets were reduced to form Na_2S and Na_2CO_3 and recycled into the fluidized bed. Flue gases derived from the fluidized bed were used to heat the drier.

98: 181418j **Paper for aqueous inks.** Jujo Paper Co., Ltd. Jpn. Kokai Tokkyo Koho JP 57,120,486 [82,120,486] (Cl. B41M5/00), 27 Jul 1982, Appl. 81/6,306, 21 Jan 1981; 6 pp. Paper is coated with binders contg. *hydroxyethyl cellulose* (I) [9004-62-0] and optionally *polyethyleneimine* [9002-98-6] and a light $CaCO_3$ pigment having sp. surface area <28,000 cm^2/g. Thus, paper coated with 25% I and 75% $CaCO_3$ (15,500 cm^2/g) had refection concn. 3.37, ink running properties A (A best, D worst) ink dot diam. 160 μ, and drying time 21 s, compared with 3.02, D, 230, and 96, resp., for using poly(vinyl alc.) as a binder.

98: 181419k **Coating compositions for offset printing of paper.** Asahi-Dow Ltd. Jpn. Kokai Tokkyo Koho JP 57,167,490 [82,167,490] (Cl. D21H1/28), 15 Oct 1982, Appl. 81/54,080, 10 Apr 1981; 12 pp. Mixts. contg. $CaCO_3$ and a copolymer of butadiene with acrylonitrile (I), a (meth)acrylic acid ester, and an ethylenic unsatd. carboxylic acid and a copolymer of vinyl acetate (II) with an ethylenic unsatd. monocarboxylic acid and a (meth)acrylic acid ester as binders are useful for coating paper for offset printing. Thus, 20 parts styrene was copolymd. with butadiene 36, I 10, Me methacrylate (III) 22, and acrylic acid (IV) 2 parts to give a copolymer (V) [41476-33-9]. II (3 parts) was copolymd. with 2 parts IV and 5 parts III in V dispersion to give alkali-sensitive latex which (10 parts) was mixed with clay 85, $CaCO_3$ 15, a dispersing agent 0.2, and oxidized starch 1 part to give a coating compn. (solids 60%) for paper.

98: 181420d **Slip prevention agents for paper.** DIC Hercules, Inc. Jpn. Kokai Tokkyo Koho JP 57,171,796 [82,171,796] (Cl. D21H1/38), 22 Oct 1982, Appl. 81/54,441, 13 Apr 1981; 9 pp. Paper coated with mixts. contg. a quaternized polymer of styrene or its deriv. with $CH_2{:}CRCO_2(CH_2)_nNR^1_3$, where R is H or Me, R^1 is Me or Et, and n is 2 or 3, and a rosin deriv., wax, or a hydrocarbon resin is slip-resistant. Thus, 72.3 parts styrene was copolymd. with 47.2 parts 2-(dimethylamino)ethyl methacrylate to give a copolymer which was quaternized with 37.8 parts di-Me sulfate in presence of 24.0 parts *Quinton B 170* [9073-70-0] to give a copolymer (I). Paper was coated (0.5 g; solids)/m^2 with I compn. (solids 20%), subsequently coated (0.5 g/m^2) with poly(vinyl alc.), and dried to give a slip-resistant paper.

98: 181421e **Coating compositions for paper.** Kanzaki Paper Mfg. Co., Ltd. Jpn. Kokai Tokkyo Koho JP 57,176,297 [82,176,297] (Cl. D21H1/22), 29 Oct 1982, Appl. 81/61,290, 24 Apr 1981; 12 pp. Paper coated with compns. contg. <80% kaolin having specified particle size and $CaCO_3$ having specified particle size and a vinyl copolymer emulsion as a binder have improved luster and smoothness. Thus, 12 parts acrylonitrile was copolymd. with butadiene 36, styrene 29, and fumaric acid 3 parts to give a copolymer (I) [29534-40-5]. Paper was prepd. and coated (two sides) with a mixt. of kaolin 20, $CaCO_3$ 80, I emulsion 12, and CM-cellulose 0.2 part to give paper with excellent luster and smoothness.

98: 181422f **Water-resistant paper.** Japan Auto Parts Industries Assoc. Jpn. Kokai Tokkyo Koho JP 57,183,498 [82,183,498] (Cl. D21H5/20), 11 Nov 1982, Appl. 81/64,680, 28 Apr 1981; 3 pp. Moisture-resistant paper is prepd. by forming paper from pulp slurries contg. *poly(vinyl alc.)* (I) [9002-89-5] and then heat-treating the paper at 145–290°. Thus, a slurry contg. carbon fibers 80, pulp 20, and I 20 parts was passed through a papermaking machine and heat-treated 2 min at 220° to give moisture-resistant paper.

98: 181423g **Polyamide fibrids.** Mitsui Toatsu Chemicals, Inc. Jpn. Kokai Tokkyo Koho JP 57,183,417 [82,183,417] (Cl. D01F6/60), 11 Nov 1982, Appl. 81/64,103, 30 Apr 1981; 8 pp. Polyamide fibrids for elec. insulating paper substitutes are prepd. by mixing a coagulating agent with a copolyamide of an arom. polycarboxylic acid with an arom. polyisocyanate at a high shear rate. Thus, 42 parts isophthalic acid was copolymd. with 2.8 parts monosodium isophthalate and 49 parts TDI to give a polyamide (I). [85528-29-6]. Aq. 40% $CaCl_2$ and I liquor were mixed at a high shear rate to give fibrids. A 1:1 (wt. ratio) mixt. of the formed fibrids and *isophthaloyl chloride-m-phenylenediamine copolymer* [25765-47-3] fibers was passed through a papermaking machine to give an elec. insulating paper substitute.

98: 181424h **Oil-resistant paper.** Sansho Co., Ltd., Osaka Jpn. Kokai Tokkyo Koho JP 57,191,399 [82,191,399] (Cl. D21H3/42), 25 Nov 1982, Appl. 81/71,185, 11 May 1981; 7 pp. Paper slurries contg. a fluoropolymer and a polysaccharide phosphate ester (I) are useful for manuf. of sized oil-resistant paper. Thus, a pulp slurry contg. 0.4% (on pulp wt.) *Asahiguard AG 530* [70407-12-4] (fluoropolymer) and 0.01% (on pulp wt.) I (*Meyprofilm 100* [78615-64-2]) was passed through a papermaking machine and dried to give a sized oil-resistant paper.

98: 181425j **Coating compositions for paper.** Mitsui Toatsu Chemicals, Inc. Jpn. Kokai Tokkyo Koho JP 57,191,392 [82,191,392] (Cl. D21H1/28), 25 Nov 1982, Appl. 81/69,351, 11 May 1981; 4 pp. Papers coated with compns. contg. a conjugated diene elastomer and a (meth)acrylonitrile copolymer emulsion have improved printing luster. Thus, 50 parts styrene was copolymd. with Me methacrylate (I) 8, butadiene 40, and acrylic acid (II) 2 parts to give an elastomer (III) [26590-06-7]. Styrene (30 parts) was copolymd. with I 10, acrylonitrile 20, Bu acrylate 55, and II 2 parts to give a copolymer (IV) [60285-50-9]. Paper was coated with a compn. contg. kaolin 90, $CaCO_3$ 10, poly(acrylic acid) Na salt 0.2, starch 5, a 60:40 (wt. ratio) mixt. of III and IV 12, and a defoamer 0.1 part, dried, and calendered at 60° to give a coated paper with high printing luster.

98: 181426k **Stabilizers for dimensional stability of paper.** Showa Denko K. K. Jpn. Kokai Tokkyo Koho JP 57,191,396 [82,191,396] (Cl. D21H3/38), 25 Nov 1982, Appl. 81/75,683, 21 May 1981; 6 pp. (Meth)acrylamide copolymers contg. units of a cationic monomer, a hydroxyalkyl (meth)acrylate or hydroxyalkyl(meth)acrylamide, and $CH_2{:}CRCO_2R^1$ (R = H or Me; R^1 = H, alkali metal, ammonium, amine, salt, or alkanolamine salt, are useful as stabilizers in the manuf. of paper having good dimensional stability. Thus, 20 parts acrylamide was copolymd. with 2-(dimethylamino)ethyl